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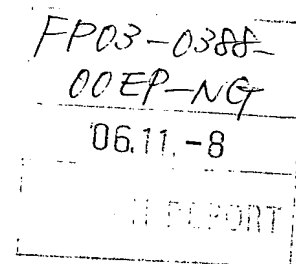
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(54) Title: **PHOSPHONIUM SALTS**

(57) Abstract: The invention provides a phosphonium salt of formula I wherein R¹, R², R³, and R⁴ are C₁₋₂₀ hydrocarbyl groups and X is an anion, except halide, provided that (i) R¹, R², R³, and R⁴ are not all the same; and (ii) not more than two of R¹, R², R³, and R⁴ are aryl. Such phosphonium salts may be useful as catalysts, solvents, and electrolytes.

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Phosphonium Salts

Field of the Invention

This invention relates to phosphonium salts and
5 particularly to such salts in the form of ionic liquids.

Background of the Invention

Ionic liquids are salts that are liquid over a broad range of temperatures. Ionic liquids are useful for many purposes, including as catalysts, solvents, and electrolytes
10 (for a general review, see Olivier, H. (1998), "Nonaqueous Ionic Liquids (NAILs)", in Aqueous Phase Organometallic Catalysis Concepts and Applications, Wiley-VCH, Chapter 7.3, pp. 554-563). Known ionic liquids are generally nitrogen-based systems. For example, U.S. Patent No. 5,731,101 (March 24,
15 1998; Sherif et al.) describes compositions comprising mixtures of a metal halide, such as aluminum trichloride (AlCl_3), and an alkyl-containing amine hydrohalide salt, such as trimethylamine hydrochloride salt ($(\text{CH}_3)_3\text{NH}^+\text{Cl}^-$) to form an ionic liquid, such as $(\text{CH}_3)_3\text{NH}^+\text{Al}_2\text{Cl}_7^-$. Pyridinium salts are
20 described by Chum et al (*J. Am. Chem. Soc.*, 97, 3264 (1975)).

Other examples of ionic liquids include 1-ethyl-3-methylimidazolium tetrachloroaluminate and 1-butylpyridinium nitrate (*Chemical & Engineering News*, March 30, 1998, pages 32 to 37), and dialkylimidazolium chloroaluminates (Wilkes, J.S.
25 et al. "Dialkylimidazolium chloroaluminate melts: A New Class of Room-Temperature Ionic Liquids for Eletrochemistry, Spectroscopy, and Synthesis" *Inorg. Chem.*, 21, 1263-1264 (1982)).

Phosphonium salts have been previously described.
30 For example, U.S. Patent No. 5,310,853, (May 10, 1994; Pham et al) describes phosphonium catalysts for use in fast cures of

epoxy resins. However, the phosphonium salts of the examples are not ionic liquids.

Summary of the Invention

In one aspect, the invention provides a phosphonium
5 salt of formula I:



wherein

R^1 , R^2 , R^3 , and R^4 each independently represents a
 C_{1-20} hydrocarbyl group, provided that (i) R^1 , R^2 , R^3 , and R^4
10 are not all the same; and (ii) no more than two of R^1 , R^2 , R^3 ,
and R^4 are aryl, and

X^- is an anion, excluding halide.

Description of the Preferred Embodiments of the Invention

R^1 , R^2 , R^3 , R^4 , and X^- are preferably chosen to obtain
15 low melting salts. If the salt is to be used as a polar
solvent for an organic reaction, then there should be chosen a
salt whose melting point is below the temperature at which the
reaction is to be carried out.

In general it is preferred that the phosphonium salt
20 of the invention is a liquid below 100°C , more preferably a
liquid below 50°C , most preferably a liquid below 35°C .

The melting point of the phosphonium salt depends
mostly upon the particular hydrocarbyl groups that are attached
to the phosphorus atom. For instance, a higher number of
25 carbon atoms present tends to result in a lower melting
product. Branching also tends to result in a lower melting
product, so it is preferred that alkyl groups are branched, for

example, α -branched or β -branched. Steric considerations may limit this, for instance, and may prohibit salts in which all of R^1 to R^4 are α -branched. Branching is especially preferred when the anion is a tosylate. Choosing R^1 , R^2 , R^3 and R^4 such
5 that they are not all the same also tends to lower the melting point of the salt.

The hydrocarbyl groups R^1 to R^4 are preferably alkyl groups but they may be, or contain, aryl groups such as phenyl, tolyl, or naphthyl groups. They may be alicyclic groups such
10 as cyclopentyl or cyclohexyl groups. They are preferably free of ethylenic unsaturation. Further, the hydrocarbyl groups may be substituted. Suitable substituents include hydroxyl and halides.

The hydrocarbyl groups can be interrupted by
15 heteroatoms that do not interfere with the utility of the phosphonium salts, or the carbon chain can bear non-interfering substituents. Which heteroatoms or which substituents interfere, of course, depends on the intended utility of the phosphonium salt and will therefore vary from case to case.
20 Oxygen is mentioned as a heteroatom that can be present in a carbon chain.

The total number of carbon atoms present in R^1 , R^2 , R^3 , and R^4 is chosen with many factors in mind but is usually 7 to 30, preferably 22 to 26 and more preferably 24.

25 Preferably, one of R^1 , R^2 , R^3 , and R^4 is a C_8 -20 alkyl group, more preferably a C_{10-16} alkyl group.

For some purposes, it is desirable that at least one of R^1 to R^4 is a long chain alkyl group containing a straight chain of at least 14 carbon atoms.

Preferably, when X is tosylate, at least one of R¹, R², R³, and R⁴ is a branched alkyl group, and two, three, or all four can be branched.

Partially fluorinated ethers are one class of R groups which can be particularly useful in certain applications. Phosphonium salts comprising one or more of such R groups tend to have high densities (for example, 1.3 to 1.5), making them well suited for phase separation. The partially fluorinated ethers may also be further substituted. An example of a partially fluorinated ether is $-(CH_2)_m-O-CH_2(CF_2)_nCF_3$ wherein n represents a number from 0 to 9, preferably 4, 6, or 8, and m represents a number from 1 to 6, preferably 3.

Other specific examples of suitable R groups include hydroxyalkyl groups, such as 3-hydroxypropyl.

As well as a being able to vary the melting points of the phosphonium salts of the invention to suit various purposes, the miscibility of the phosphonium salts with organic compounds can be extensively varied, particularly by altering the chain lengths of the R groups. This feature can be quite useful in carrying out a chemical reaction. For instance, in a reaction where the salt is used as a polar solvent, the salt may be selected because it is miscible with a product of the reaction at elevated temperature but immiscible at a lower temperature. In this example, upon termination of the reaction, the reaction mixture can be cooled to the lower temperature to result in two liquid phases and the product phase simply decanted off. This lower temperature is preferably ambient temperature. Alternatively, if the salt is miscible with the product at the lower temperature, one possibility to separate the product from the salt is to boil off the product, leaving the solvent ready to be used again. In general, the longer the hydrocarbyl groups are, the greater

the miscibility with organic reactants and products. With shorter hydrocarbyl groups, the product and/or reactant may become miscible with the phosphonium salt upon heating.

The phosphonium salt can be selected with the
5 required properties as a solvent in mind.

As there are four groups, R^1 , R^2 , R^3 and R^4 , that can be varied, the phosphonium salts display a high degree of flexibility that assists in selecting particular properties of the salt, such as the melting point. This contrasts, for
10 instance, with the known imidazolium salts mentioned above, which have only two groups that can be varied. It also contrasts with ammonium salts. Although ammonium salts bear four groups attached to one nitrogen atom, in practice the ammonium salts are made from tertiary amine precursors, and it
15 is difficult to make mixed tertiary amines. Hence the ammonium salts that are practically available are confined to those which have three identical and one different group attached to the nitrogen atom, so their flexibility is limited.

It is not difficult to prepare phosphonium salts
20 bearing different groups, giving a higher degree of flexibility. Tertiary phosphines can be prepared by reacting phosphine with an olefin or a mixture of olefins. For example, if phosphine is reacted with a mixture of hexene and octene there is obtained a mixture of four tertiary phosphines,
25 namely, trihexyl, trioctyl, dihexyloctyl and dioctylhexyl phosphines. This provides additional flexibility in tailoring the tertiary phosphine and, subsequently, the phosphonium salt to have particular selected properties.

Suitable anions, X, include phosphate, nitrate,
30 hexafluorophosphate (PF_6^- , SbF_6^-), tetrafluoroborate, (BF_4^-) tetrachloroaluminate ($AlCl_4^-$), $Al_2Cl_7^-$, carboxylates, and

sulfonates. Examples of sulfonates include tosylate, mesylate, benzenesulfonate, and triflate. Examples of carboxylates include acetate, propionate, and trifluoroethanoate. Preferred anions are sulfonates, tetrafluoroborate, hexafluorophosphate, 5 SbF_6^- , AlCl_4^- and Al_2Cl_7^- . Especially preferred are tosylate, tetrafluoroborate, and hexafluorophosphate.

The anion, X, also affects the properties of the phosphonium salt, including the melting point. Many anions are available but the required properties of the phosphonium salt 10 should be borne in mind when selecting the anion.

As examples of liquid phosphonium salts there are mentioned triisobutylmethylphosphonium tosylate and diisobutyl-n-octylmethylphosphonium tosylate, both of which are liquids at room temperature. The compound tri-n-butylmethyl-phosphonium 15 tosylate is a high melting solid. The distinction in melting point between the tri-n-butyl compound and the corresponding triisobutyl compound is a clear demonstration of the effect of branching on the melting point of the compound.

Ionic liquids of the invention are also suitably 20 formed from mixtures of phosphonium salts of formula I.

The phosphonium sulfonates of the invention can readily be prepared by reacting a tertiary phosphine $\text{R}^1\text{R}^2\text{R}^3\text{P}$ with a sulfonate ester R^4X , where R^1 , R^2 , R^3 and R^4 are as defined above, and X is a sulfonate. A mixture of different 25 tertiary phosphines can be used. The reaction proceeds readily at elevated temperature, say 60 to 100°C, and is often complete in about 4 to 5 hours. For instance, phosphonium tosylates are readily prepared by heating a tertiary phosphine with a tosylate ester, suitably a lower alkyl tosylate ester, to form 30 a phosphonium tosylate.

In cases where the anion is other than a sulfonate, it is convenient to first prepare the corresponding halide salt, by combining a tertiary phosphine $R^1R^2R^3P$ with an alkyl halide under conditions similar to those given above for
5 tosylates. For instance, there may readily be prepared a phosphonium chloride, by reaction of a tertiary phosphine with a lower alkyl chloride.

Phosphonium hexafluorophosphates and tetrafluoroborates are typically prepared through an anion
10 exchange process from a halide salt such as the chloride or bromide salt.

In some instances it is convenient to then convert the phosphonium halide, by anion exchange, to the desired phosphonium salt. For instance, to prepare phosphonium
15 hexafluorophosphate or tetrafluoroborate from the phosphonium chloride, an anion exchange is done with the corresponding phosphonium chloride and hexafluorophosphoric acid, e.g. in a 60% aqueous solution in water as solvent, or sodium tetrafluoroborate in acetone as solvent. To make the
20 carboxylate, phosphate, sulfate, nitrate, or acetate salts, the corresponding phosphonium chloride is mixed with sodium hydroxide in methanol. Sodium chloride falls out of solution. The resulting phosphonium hydroxide is mixed with the acid corresponding to the desired salt (i.e. a carboxylic acid is
25 used to form a phosphonium carboxylate) to obtain the desired product.

To form the tetrachloroaluminate, a phosphine is mixed with trichloroaluminum.

Trace levels of halide ion usually remain in the
30 phosphonium salt when converting a phosphonium halide to another salt. If such converted salts are to be used in an

environment where halide ions are unacceptable, even at low levels, phosphonium halides should not be used as starting materials, or a process must be used which ensures complete removal of halide ions. For instance, halide ions such as chloride ions coordinate with group VIII metals such as palladium and platinum. If the phosphonium salt is to be used as a solvent for a reaction that is catalysed by a palladium or platinum catalyst the phosphonium salt must be totally free of halide anion. Sulfonates would be preferred in such cases.

Halide ions do not coordinate with nickel, so if the phosphonium salt is to be used as a solvent for a nickel-catalysed reaction it is acceptable that trace levels of halide ion remain.

The phosphonium salts of the invention are very thermally stable. They have extremely low vapour pressure and may decompose rather than boil. The temperature at which this occurs will vary from compound to compound, but substantially all are stable up to about 200°C, many are stable up to about 300°C and some are stable even up to about 450°C. These properties render them useful for many purposes, but particularly for use as a solvent for various reactions including carbonylation, hydrogenation, hydroformylation, olefin dimerization, olefin oligomerization, olefin polymerization, acylation, alkylation, reduction and oxidation reactions. For instance the reaction of carbon monoxide, ethylene and methanol or ethanol in the presence of a palladium catalyst to form methyl acetate or ethyl acetate, respectively, can be carried out in a phosphonium salt of the invention as solvent, and the product ester distilled off thereafter.

The invention is further illustrated in the following examples.

Example 1Preparation of triisobutylethylphosphonium tosylate:

An inerted reactor was charged with ethyl tosylate. After heating the tosylate ester to 100-110°C, a 2-3% molar excess of triisobutylphosphine was added slowly over 1-2 hours. The reaction was exothermic and the temperature of the reaction was controlled by regulating the addition rate and by removing the source of heat. After a two hour digestion period the mixture was cooled to 50°C at which point enough dilute aqueous hydrogen peroxide was added to convert the excess triisobutylphosphine (less than 0.5%) to the corresponding phosphine oxide. The product mixture was then vacuum stripped to remove the water. The triisobutylethylphosphonium tosylate product was a solid (mp 28-29°C) but it could be supercooled and thus remain a liquid at 10-12°C. Above 30°C, it was a viscous liquid and its viscosity decreased rapidly with increasing temperature. It was more dense than water (approximately 1.06 g/cc at 30°C).

Example 2Preparation of triisobutylmethylphosphonium tosylate:

The procedure of Example 1 was followed, except that methyl tosylate was used in place of ethyl tosylate. The triisobutylmethylphosphonium tosylate product that was obtained from the vacuum stripping was a viscous liquid at room temperature but its viscosity decreased rapidly with increasing temperature. Its density was approximately 1.065/cc at 30°C.

Examples 3 to 12

Alkylphosphonium tosylates listed in Table 1 were synthesized in a manner similar to that described for Examples 1 and 2.

Table 1: Alkyl Phosphonium Tosylates

Example	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>R⁴</u>	<u>m.p.</u> <u>(C)</u>	<u>Density (g/mL)</u>	
						<u>30°C</u>	<u>60°C</u>
8	Et	Et	Et	Et	68-69	-	-
9	n-Pr	n-Pr	n-Pr	Me	50-52	0.9974	0.9802
10	n-Pr	n-Pr	n-Pr	Et	52-53	-	-
11	n-Bu	n-Bu	n-Bu	Me	72-73	-	-
12	n-Bu	n-Bu	n-Bu	Et	71.5- 73.5	-	-
2	iBu	iBu	iBu	Me	liquid ²	1.0664	1.0486
1	iBu	iBu	iBu	Et	28-29	1.0593	1.0416
3	iBu	iBu	octyl	Me	<40	1.0229	1.0036
4	iBu	iBu	octyl	Et	liquid ²	1.0148	0.9955
5	iBu	iBu	tetradecyl	Me	<40	0.9885	0.9681
6	iBu	iBu	tetradecyl	Et	liquid ²	0.9821	0.9619
7	Mixed Hexyl/Octyl ¹			Me	<40	0.9853	0.9661

5

¹The phosphonium salts were prepared from a mixture of phosphines (R¹R²R³P), wherein R¹, R², and R³ are each hexyl or octyl.

10

²At Room Temperature.

Example 13

Preparation of tri-hexyl(tetradecyl)phosphonium hexafluorophosphate: 202 g of tri-hexyl(tetradecyl)phosphonium chloride was dissolved in 293 g of distilled water. To this solution 99.4 g of 60% aqueous hexafluorophosphoric acid was added with stirring at room temperature. A waxy immiscible solid formed. After two hours of stirring, the mixture was warmed to 45°C. At this point there were two liquid layers. The aqueous layer was decanted and the organic phase was washed two times with two volumes of distilled water at 45°C to remove residual HCl. Finally the organic phase was heated to 100°C under 20 mmHg pressure to remove the last traces of water. 238 g of a low melting (29-33°C) product was recovered.

Examples 14 to 21

Alkylphosphonium hexafluorophosphates listed in Table 2 were synthesized in a manner similar to that described for Example 13. Example 21 is provided for the purpose of comparison.

Table 2: Alkyl Phosphonium Hexafluorophosphates

Example	R ¹	R ²	R ³	R ⁴	m.p. (C)	P NMR (ppm)		F NMR (ppm)
						<u>R₄P</u>	<u>PF₆</u>	
16	Propyl	Propyl	Propyl	Tetradecyl	44.5-45.5	32.46	-143.67	-69.22 -73.02
15	Butyl	Butyl	Butyl	Tetradecyl	38.0-39.0	33.75	-143.54	-69.83 -73.61
14	Pentyl	Pentyl	Pentyl	Tetradecyl	35.5-37.0	33.55	-143.68	-69.18 -72.97
13	Hexyl	Hexyl	Hexyl	Tetradecyl	29-33	33.53	-143.68	-69.93 -73.7
21	Butyl	Butyl	Butyl	Butyl	161-163	34.47	-143.32	-70.47 -74.25
17	Dodecyl	Dodecyl	Dodecyl	Dodecyl	72-78	33.2	143.47	-69.5 -73.28
18	Mixed Butyl/Hexyl ¹	Mixed Butyl/Hexyl ¹	Mixed Butyl/Hexyl ¹	Tetradecyl	liquid/solid ²	33.4	-143.75	-69.89 -73.67
19	Mixed Butyl/Octyl ¹	Mixed Butyl/Octyl ¹	Mixed Butyl/Octyl ¹	Butyl	<30	34.36	-143.36	-70.45 -74.21
20	Mixed Hexyl/Octyl ¹	Mixed Hexyl/Octyl ¹	Mixed Hexyl/Octyl ¹	Octyl	55.5-64.0	33.45	-143.85	-70.11 -73.39

¹The phosphonium salts were prepared from a mixture of phosphines (R¹ R² R³P), wherein R¹, R², and R³ are each one of the two components listed.

²At Room Temperature.

Example 22

Preparation of tri-hexyl(tetradecyl)phosphonium tetrafluoroborate: A stirred reactor was charged with two parts of acetone and one part by weight of tri-hexyl (tetradecyl)phosphonium chloride. To this solution was added a 50% molar excess of sodium tetrafluoroborate. The mixture was stirred vigorously for 10 minutes at room temperature. Afterwards, it was filtered to remove the excess sodium tetrafluoroborate and precipitated sodium chloride. The clear acetone solution containing tri-hexyl(tetradecyl)phosphonium tetrafluoroborate was then heated under reduced pressure to remove the acetone. The final conditions were 140°C at 0.3 mmHg pressure. The product was slightly viscous pale yellow oil which had a melting point of 30°C. The chloride content was 0.16%. This represents approximately 98% conversion of the chloride to tetrafluoroborate.

Examples 23 and 24

Alkylphosphonium tetrafluoroborates listed in Table 3 were synthesized in a manner similar to that described for Example 22.

Table 3: Alkyl Phosphonium Tetrafluoroborates

<u>Examples</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>R⁴</u>	<u>m.p. (C)</u>	<u>P NMR (ppm)</u> <u>R₄P</u>	<u>F NMR (ppm)</u> <u>BF₄</u>	<u>B NMR (ppm)</u> <u>BF₄</u>
23	Butyl	Butyl	Butyl	Tetradecyl	32-35	33.83	-153.74	-0.7224
22	Hexyl	Hexyl	Hexyl	Tetradecyl	liquid ²	33.32	-149.09	-1.021
24	Mixed Butyl/Hexyl ¹			Tetradecyl	liquid	33.45		-1.1602

¹The phosphonium salts were prepared from a mixture of phosphines (R¹ R² R³P), wherein R¹, R², and R³ are each butyl or hexyl.

²At Room Temperature.

Example 25

Preparation of diisobutyl(methyl)(3-(1,1-dihydroperfluorooctoxy)propyl)phosphonium tosylate: A stirred reactor was charged with one equivalent of methyltosylate.

5 After heating the tosylate ester to 100°C, one equivalent of diisobutyl(3-(1,1-dihydroperfluorooctoxy)propyl)phosphine was added over 2 hours. The mixture was held for an additional 6 hours at 100°C. The product was a viscous liquid at room temperature, with a density and viscosity of 1.34 g/cc and 5.8

10 cps, respectively, at 60°C.

Example 26

Preparation of bis(3-(1,1-dihydroperfluorooctoxy)propyl)(isobutyl)(methyl)phosphonium tosylate: A stirred reactor was charged with one equivalent of methyltosylate.

15 After heating the tosylate ester to 100°C, one equivalent of bis(3-(1,1-dihydroperfluorooctoxy)propyl)(isobutyl) phosphine was added over 2 hours. The mixture was held for an additional 6 hours at 100°C. The product was a viscous liquid at room temperature, with a density and viscosity of 1.5 g/cc and 50

20 cps, respectively, at 60°C.

Example 27

The miscibility of phosphonium iodides with dodecane as a function of number of carbons in a series of phosphonium iodides was determined. While phosphonium iodides are not part

25 of the claimed invention, this example is provided here to demonstrate how miscibility may be affected by carbon number for phosphonium salts. The first column of Table 4 identifies the tertiary phosphine, most of which have R groups which are a mixture of different lengths. Column 2 identifies the alkyl

30 iodide with which the tertiary phosphine has been reacted to form a phosphonium iodide. Column 3 shows the average number

of carbon atoms per phosphonium iodide molecule and column 4 shows the average molecular weight of the phosphonium iodide products. The last column shows the temperature at which the phosphonium iodide became miscible with dodecane.

- 5 This Table demonstrates that the miscibility of the phosphonium iodides with dodecane decreases as the number of carbon atoms in the phosphonium iodide increases.

Table 4: Miscibility of Phosphonium Iodides with Dodecane

R ³ P	R ¹	Carbon No.	Ave. MWt.	MP (C)	Miscib. Temp
C ₆ /C ₈ ¹	C ₄	24.9	506.6	Liquid ²	>162
C ₆ /C ₈ ¹	C ₆	26.9	534.6	Liquid ²	>162
C ₆ /C ₈ ¹	C ₈	30.9	590.6	Liquid ²	162
C ₆ /C ₈ ¹	C ₁₀	32.9	618.6	Liquid ²	132
C ₈ /C ₁₂ ¹	C ₄	33.5	627	31	125
C ₁₀ /C ₁₂ ¹	C ₄	34.8	645.2	27	102
C ₈ /C ₁₂ ¹	C ₆	35.5	655	42	110
C ₈ /C ₁₂ ¹	C ₈	37.3	680.2	54	71
C ₁₀ /C ₁₂ ¹	C ₆	38.8	701.2	42	83
C ₁₀	C ₁₀	40	718	Liquid ²	57
C ₁₂	C ₄	40	718	Liquid ²	43
C ₁₂	C ₆	42	746	Liquid ²	34
C ₁₂ /C ₁₄ ²	C ₄	42.8	757.2	46	37

¹The phosphonium salts were prepared from a mixture of phosphines (R¹ R² R³P), wherein R¹, R², and R³ are each one of the two components listed.

5 ²At Room Temperature

CLAIMS:

1. A phosphonium salt of formula I
- $$\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{P}^+ \text{X}^-$$
- 5 wherein R^1 , R^2 , R^3 and R^4 are C_{1-20} hydrocarbyl groups and X is an anion, excluding halide, provided that
- (i) R^1 , R^2 , R^3 and R^4 are not all the same; and
- (ii) not more than two of R^1 , R^2 , R^3 and R^4 are aryl.
2. The salt according to claim 1, wherein the sum total
10 of the carbon atoms present in R^1 , R^2 , R^3 and R^4 is from 7 to 30 inclusive.
3. The salt according to claim 1 or 2, wherein at least two of R^1 , R^2 , R^3 and R^4 are different from the others of R^1 , R^2 , R^3 and R^4 .
- 15 4. The salt according to claim 1, 2, or 3, wherein one of R^1 , R^2 , R^3 and R^4 includes a straight chain of 14 or more carbon atoms.
5. The salt according to any one of claims 1 to 4, wherein R^1 , R^2 , R^3 and R^4 are all saturated acyclic groups.
- 20 6. The salt according to any one of claims 1 to 5, wherein at least one of R^1 , R^2 , R^3 , and R^4 is a partially fluorinated ether.
7. The salt according to claim 6, wherein at least one of R^1 , R^2 , R^3 , and R^4 is $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2(\text{CF}_2)_n\text{CF}_3$, wherein n
25 is 4, 6, or 8.

8. The salt according to any one of claims 1 to 7, wherein at least one of R^1 , R^2 , R^3 , and R^4 is a hydroxyalkyl group.

9. The salt according to claim 8, wherein at least one
5 of R^1 , R^2 , R^3 , and R^4 is 3-hydroxypropyl.

10. The salt according to any one of claims 1 to 5, wherein the anion is selected from the group consisting of sulfonates, tetrafluoroborate, hexafluoroborate, SbF_6^- , $AlCl_4^-$,
10 and $Al_2Cl_7^-$.

11. The salt according to any one of claims 1 to 10 having a melting point below $100^\circ C$.

15 12. The salt according to any one of claims 1 to 10 having a melting point below $50^\circ C$.

13. The salt according to any one of claims 1 to 10 having a melting point below $35^\circ C$.

20

14. Use of a phosphonium salt according to any one of claims 1 to 13 as a reaction solvent.

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al Application No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F9/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	LUDLEY P ET AL: "Phosphonium tosylates as solvents for the Diels-Alder reaction" TETRAHEDRON LETTERS, vol. 42, no. 10, 4 March 2001 (2001-03-04), pages 2011-2014, XP004238666 ISSN: 0040-4039 Salts A and B	1-3,5, 10-14
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

27 July 2001

Date of mailing of the international search report

03/09/2001

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X	KARODIA ET AL: "Clean catalysis with ionic solvents - phosphonium tosylates for hydroformylation" CHEMICAL COMMUNICATIONS, no. 21, 1998, pages 2341-2342, XP002172927 ISSN: 1359-7345 Salt 4	1-3,5, 10-14
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